

Flame Retardancy of Chemically Modified Lignin as Functional Additive to Epoxy Nanocomposites

John A. Howarter^{1,2}, Gamini P. Mendis¹, Alex N. Bruce¹, Jeffrey P. Youngblood¹, Mark A. Dietenberger³,
Laura Hasburgh³

¹*Materials Engineering, Purdue University, West Lafayette, IN 47907*

²*Environmental & Ecological Engineering, Purdue University, West Lafayette, IN 47907*

³*USDA Forest Service, Forest Products Laboratory, One Gifford Pinchot Drive, Madison, WI 53726-2398, USA*

howarter@purdue.edu, mdietenberger@fs.fed.us

I: INTRODUCTION

Epoxy printed circuit boards are used in a variety of electronics applications as rigid, thermally stable substrates. Due to the propensity of components on the boards, such as batteries and interconnects, to fail and ignite the epoxy, flame retardant additives are required to minimize fire risk. Currently, industry uses brominated flame retardants, such as TBBPA, to meet regulatory requirements¹. However, recently, a number of environmental and human health issues have been raised about brominated compounds, so there is a desire to develop alternative flame retardant chemistries.

Phosphorus-based compounds, such as triphenyl phosphate (TPP)^{2,3} and 9,10-dihydroxy-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO)⁴, have been examined as possible alternatives to brominated flame retardants. Phosphorus-based compounds generally work by forming phosphoric acid, which works in both the vapor phase to remove radicals and the condensed phase to promote char formation⁵. Further synergistic effects have been seen with nitrogen containing polymers, where a glassy phosphorous-nitrogen layer is formed⁵. Phosphorus compounds, especially additive chemistries, may have some negative environmental impacts as they are able to diffuse out of the polymer, bioaccumulate and cause aquatic toxicity¹.

To avoid toxicity issues, it is possible add phosphorus functionality onto other molecules which are less able to diffuse out of the epoxy. One possible alternative material is lignin. Lignin is a renewable, high molecular weight, phenolic wood derivative produced as a byproduct of the paper industry⁶. It has been shown to have natural char forming properties and to increase flame retardancy in some polymer systems⁷⁻⁹.

In this work, we aim to examine the interaction between the epoxy, phosphorus compounds and the lignin to decrease the flammability. The system is characterized through the use of scanning electron microscopy, thermogravimetric analysis and mass loss calorimetry¹⁰.

II. MATERIALS AND METHODS

A. *Phosphorylated lignin synthesis:*

A 500mL round bottom flask, a condenser and 60 g of kraft lignin (Sigma Aldrich, St. Louis, MO) were dried at 110°C for 3 hours to remove water. 50 g of dried lignin was measured into the round bottom, which was then capped with the condenser and a rubber septa. While stirring, 50mL of anhydrous N,N-dimethylformamide (DMF) (Sigma Aldrich, St. Louis, MO) was added slowly to dissolve the lignin. The DMF-lignin solution was subjected to three freeze-pump-thaw iterations to remove any residual air contamination. The glassware was heated to 150°C using a silicone oil bath, with the condenser active, under flowing N₂ gas. Diphenylphosphorylchloride (DPC) (Sigma Aldrich, St. Louis, MO) was added in 2mL increments every minute until 100mL were dispensed. Upon addition, a white gas was evolved and the temperature of the solution increased, and DMF condensation became significant. After 18 hours, the reaction was terminated with 100mL of methanol (Sigma Aldrich, St. Louis, MO) and was removed from

heat. The solution was washed with water, filtered using filter paper and re-dispersed in DMF and reprecipitated in water three times to remove excess DPC. The resulting brown powder was dried at 110°C to remove excess water.

TABLE I: Composite compositions

Sample Name	DGEBA (Vol %)	TETA (Vol%)	Filler 1 (Vol %)	Filler 2 (Vol %)
Neat Epoxy	89.5	10.5	-	-
Neat Lignin	71.6	8.4	20-Lignin	-
TPP	71.6	8.4	20-TPP	-
Lignin + Cloisite	71.6	8.4	10- Lignin	10- Cloisite
Phos. Lignin	71.6	8.4	10- Phos. Lignin	-

B. Composite fabrication

Triphenyl phosphate (TPP) (Sigma Aldrich, St. Louis, MO), unmodified (neat) kraft lignin, Cloisite 15 (Southern Clay Products, Gonzales, Texas) and phosphorylated lignin were used as potential flame retardant filler materials in epoxy composites. Epoxy samples were fabricated using compositions found in Table I. EPON 825 resin (Momentive, Garrett, IN) and the filler materials were added together and were mixed using a SpeedMixer (FlackTek Inc., Landrum, South Carolina), at 2000rpm for 30 seconds, removed and cooled in an ice bath for 30 seconds, mixed again at 2000rpm for 30 seconds. Triethylenetetramine (Sigma Aldrich, St. Louis, MO) was added and incorporated by hand before mixing in the SpeedMixer at 2000 rpm for 30 seconds, cooling in an ice bath for one minute, then mixing at 2000rpm for another 30 seconds, to minimize viscous heating and prevent unintentional curing. The samples were massed into Mold Max silicone molds (Smooth-On, Macungie, PA) and cured, covered, at room temperature for 12 hours, then was cured at 100°C for 2 hours, post cured at 120°C for 2 hours, then cooled to 80°C over 2 hours. The epoxy samples were sectioned using a water cooled abrasive saw and ground to dimensions using a belt sander. Final dimensions of the samples were 100mm by 100mm by 5.8±0.3mm.

C. Characterization

SEM samples were sectioned using an abrasive saw and polished in sequence of finer grits, ending with 3µm diamond paste. Samples were then cleaned with water, acetone and methanol and sputtered with gold-palladium for 120 seconds using a sputter coater (Structure Probe Inc., West Chester, Pennsylvania) to increase surface conductivity. Images were taken using an XL-40 SEM (FEI, Hillsboro, Oregon) at a 5kV accelerating voltage.

Thermogravimetric Analysis was conducted using a Q50 TGA (TA Instruments, New Castle, Delaware) in a 60mL air/40mL N₂ mix at a heating rate of 20°C/min from ambient to 1000°C. Alumina crucibles pans were used to prevent the formation of a Pt-P eutectic and subsequent pan melting.

Heat release rate and mass loss rate was measured using a Mass Loss Calorimeter (Fire Testing Technology, East Grinstead, West Sussex, UK) with a heat flux of 35 kW/m². The heat release rate was calibrated using poly(methyl methacrylate) and polyethylene glycol standards, from which constants were extrapolated and used to fit the thermopile data. A Savitzky-Golay filter was applied to reduce noise in the mass loss data. Samples were wrapped in copper foil prior to testing, due to previously observed

degradation of the standard aluminum foil during combustion. The test was stopped when the mass loss rate remained below 2.5 g/s for 5 seconds.

III: RESULTS AND DISCUSSION

A: Microstructure of epoxy composites

SEM micrographs (Figure 1) indicate dense, homogeneous, non-porous samples in both the Neat epoxy and TPP samples. The lignin-containing samples exhibited a homogeneously distributed, second phase morphology with some porosity, possibly due to particle pullout during sample preparation. The lignin + cloisite sample exhibited intercalation of the clay particles, with some interplanar debonding between clay layers. The phos. lignin specimen exhibited a bimodal size distribution of second phase particles.

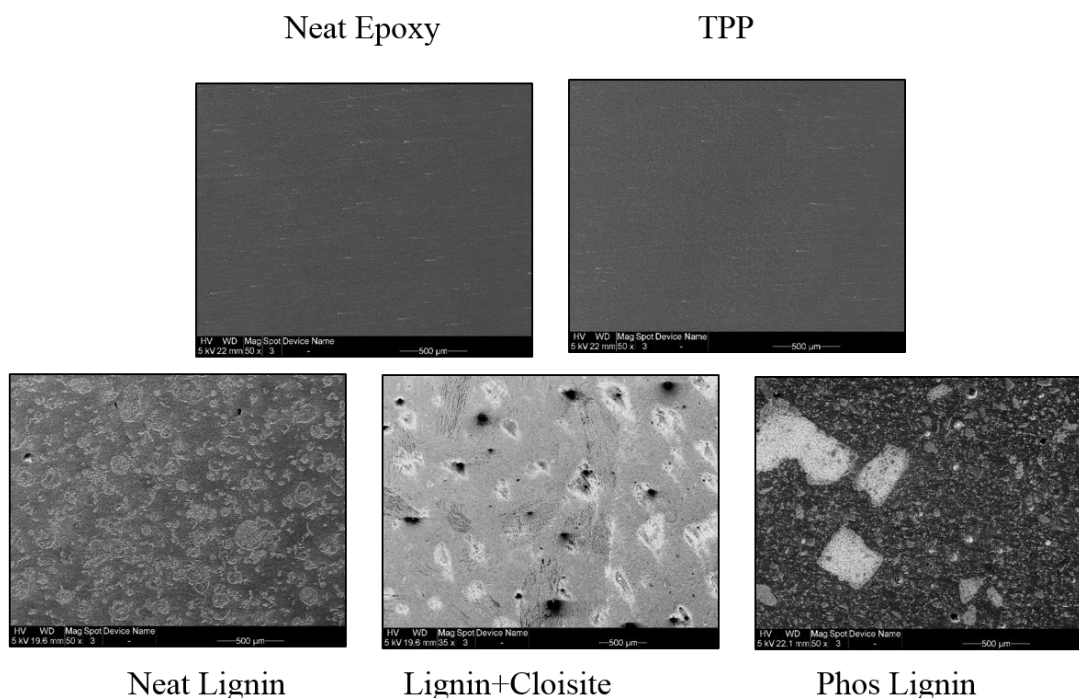


Figure 1: SEM images of epoxy composite microstructures. The TPP sample exhibits complete solubility while the lignin and clay samples contain second phase particles.

B. Ignition time

The ignitability of the samples is dependent on the combustibility of volatile compounds emerging from the sample. The neat epoxy sample took the longest time to ignite, due to a limited amount of volatiles coming off the surface of the sample. As seen in Figure 2, the lignin-containing samples were shown to ignite first. This first decomposition is likely due to the degradation of the aliphatic alcohols and carboxylic acid functionalities of the lignin¹¹. Unusually, char formation begins in both the lignin and phos. lignin samples before ignition. The TPP sample emitted volatiles very early in the test, but did not ignite until after the phos lignin and lignin + cloisite samples.

TABLE II: Modes of thermal decomposition of epoxy composites.

	Warping	Bubbling	Smoking	Charring	Intumescence
Neat Epoxy	Y	Y	Y, early	Y, not dense	N
Neat Lignin	Y	Y, after ignition	Y, early, lots	Y, before ignition	Y, intermediate
TPP	Y	Y, shortly before ignition	Y, early	Y	Y, significant
Lignin + Cloisite	N, not visible	N	Y, early	Y, after ignition	Y, minimal
Phos Lignin	Y	N	Y, shortly before ignition	Y, before ignition	Y, minimal

B. Heat release behavior and char formation

The neat epoxy combustion progressed rapidly after ignition, in a manner consistent with an intermediately thermally thick sample, and forming relatively small, inhomogeneous islands of char over the surface of the sample. The appearance of a second peak/shoulder in Figure 2 is expected to be due to the degradation of previously shielded material underneath the sides of the specimen holder. The total amount of heat released in the epoxy sample was the greatest, and the residual mass at the end of the test was the lowest, due to the inability of the epoxy to form significant amounts of char or intumescent material.

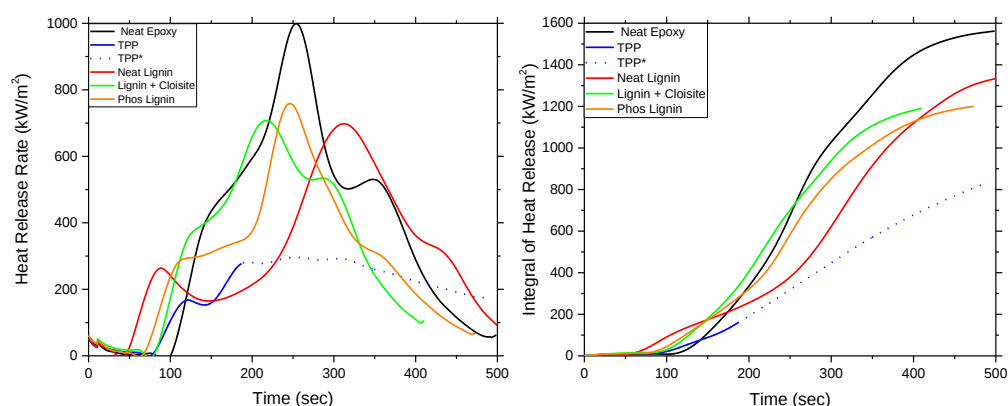


Figure 2: Heat release rate (left) and total heat release (right) of epoxy samples tested using a mass loss calorimeter.

The TPP sample exhibited early mass loss, likely due to evaporation of the TPP or the breaking of the P-O bond and the volatilization of phenol from the sample. The sample ignited before the Neat Epoxy sample, but exhibited large amounts of intumescence (>25x original volume), and clogged up the thermopile column. This event is indicated on the graphs by a transition from a solid blue line to a dotted blue line. At this point, the sample has expanded to such an extent that it impinges on the heaters, presses down upon the scale and occludes the thermopile column. Here, the thermopiles measuring heat release and the mass balance measuring mass loss begins to record unphysical data. Video evidence of this can be obtained upon request. As the data could not be validated, the peak heat release and mass losses shown can only be used as a poor approximation of the actual behavior of the material. Perhaps the excessive intumescent resulted from combining strong blowing agents from both TPP phenols and epoxy volatiles that expanded the liquified epoxy into bubble-like structures just prior to its charring by the phosphate ion. Further experimentation will be conducted to provide a better understanding of this behavior.

The neat lignin sample emitted flammable volatiles at a similar time to the other samples, but proceeded to combust earlier. Rapid formation of char on the surface of the sample is evident in the heat release rate data, as demonstrated by the initial peak and subsequent decrease in the heat release rate. Due to the formation of a thick intumescent/char layer, the peak of the heat release rate curve broadened and decreased and the total heat released in the early stages of combustion are low, as shown in Figure 2. To form the thick intumescent it could be that the epoxy locally degrades and volatilizes to provide the blowing agents to bubble the liquified lignin before it self-chars. However the total amount of heat released was the greatest of the modified samples. This is thought to be due to smoldering decomposition of the char after the combustion of the epoxy largely finishes.

The lignin + cloisite sample exhibited epoxy-like curve behavior at an earlier time, indicating that the char formation was not a successful diffusion barrier. However, by lowering the amount of combustible material in the sample, the total heat released was lowered and combustion ended much earlier. During the test, it was noted that small flaming pieces of the sample were emitted, possibly by entrapped gasses between the clay particles. At the end of the test, the residual char was found to be cracked, exposing the copper sheet at the bottom in several places. The mass fraction of the sample remaining at the end of the test was not as high as expected, considering that an additional 10 vol% of inflammable material was added. This may suggest that the cloisite actually decreases the effective amount of char formed by the lignin/epoxy.

The phosphorylated lignin exhibited an intermediate ignition time between the neat lignin and the neat epoxy. More interestingly, between 100 seconds and 200 seconds the heat release rate curve flattened, and the sample quickly formed a dense char layer. After the formation of this char layer, heat release was dominated by epoxy-like behavior. In this regime, the epoxy acted as a blowing agent, expanding somewhat the apparent volume of the char. From this observation, it is thought that the phosphorylated lignin particles degrade and form char at a self-similar temperature, and that the char is formed through the propagation of the thermal wave (~70s) through the epoxy. After the lignin particles have formed char, the epoxy is able to combust normally.

D. Thermogravimetry comparison

TGA data (Figure 3) was obtained to examine how the polymer decomposed in the absence of combustion. All samples degraded rapidly to around 70% mass loss just below 400°C due to the major epoxy component and then a slow degradation above 400°C due to some char-like behavior that was not permanent for the most part. The TPP sample began to degrade first, likely through the decomposition of the P-O bonds in the TPP molecule. It then formed a thermally stable char that remained until very high temperatures. The neat lignin and lignin + cloisite samples decomposed at higher temperatures than the neat epoxy and formed intermediate levels of char in the 400-600°C range. The lignin+ cloisite sample contained 10 vol% of the cloisite inorganic filler that would not decompose in the temperature ranges tested. The phos lignin and the neat epoxy degraded at the same temperature, however the phos lignin formed ~15 wt% more char at intermediate temperatures. This char decomposed into phosphorous-based residue around 750°C. Due to the small sample size in the TGA, the test is only able to show the enhancing lignin effect on charring during specific temperature ranges, but is not able to show how a char layer thermally protects the underlying thick material from degradation or delays its degradation.

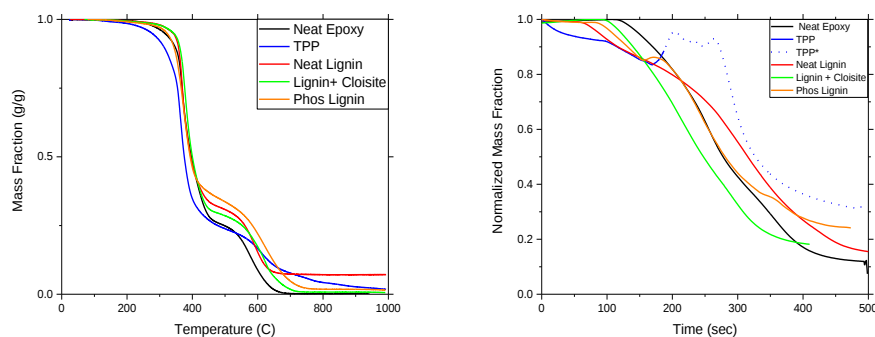


Figure 3: Thermogravimetric (left) and mass loss calorimetry (right) data of degradation of epoxy composites.

E. Char formation

The epoxy composites formed distinctly different char morphologies in the MLC tests of samples exposed to 35 kW/m^2 and flaming heat flux as shown in Figure 3. The early part of the MLC test tends to mimic the TGA test (taking into account differing temperature rise rates), but because of the thermal insulating effect of char or intumescent, the whole of a MLC test can reveal additional features. The neat epoxy and the lignin+cloisite specimen did not form a cohesive char layer to cover the entire surface of the sample. The TPP, neat lignin and phos lignin samples created solid barrier layers. The intumescent char formed by the lignin and TPP samples was fragile and well foamed, while the phos lignin formed a dense, approximately 5mm thick dome of char, below which, little material remained.

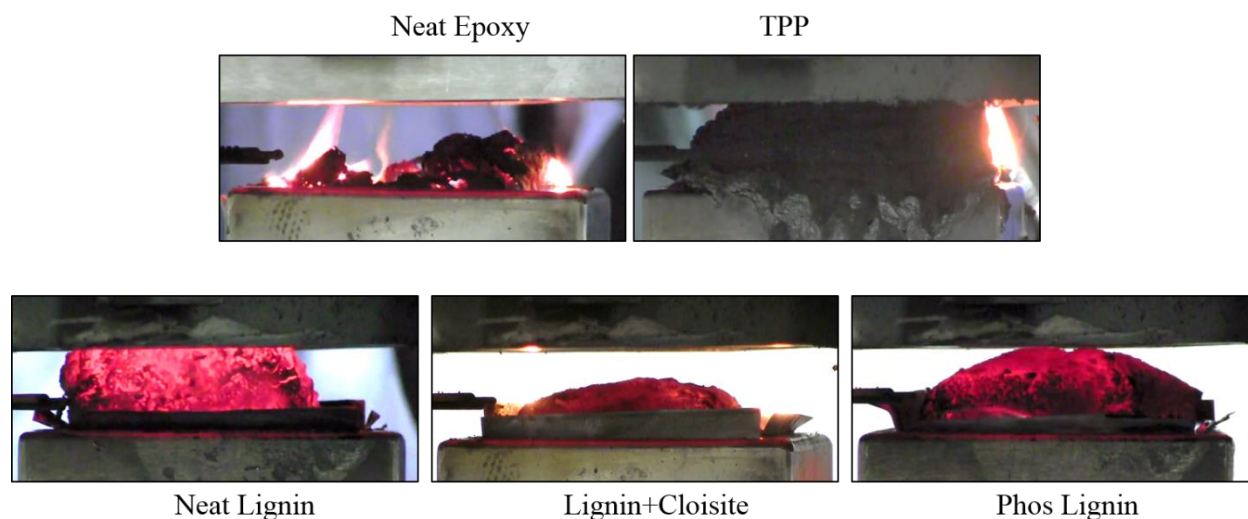


Figure 3: Optical images of the char formed during the mass loss calorimetry tests.

Interestingly, intumescence was not seen in the phosphorylated lignin sample, even though intumescence was observed in both the neat lignin and the triphenyl phosphate samples. One possible explanation is that diphenyl phosphoryl chloride stabilizes compounds that would normally have degraded and volatilized off of the sample. Instead of volatilizing, remnants of these compounds might still be found in

further analysis of the char. Another possible explanation is that the phosphate remains trapped in the modified lignin during the low temperature degradation of the epoxy matrix and becomes only available at higher temperatures in assisting the lignin to form a dense char layer with minimal intumescent behavior.

IV. CONCLUSIONS:

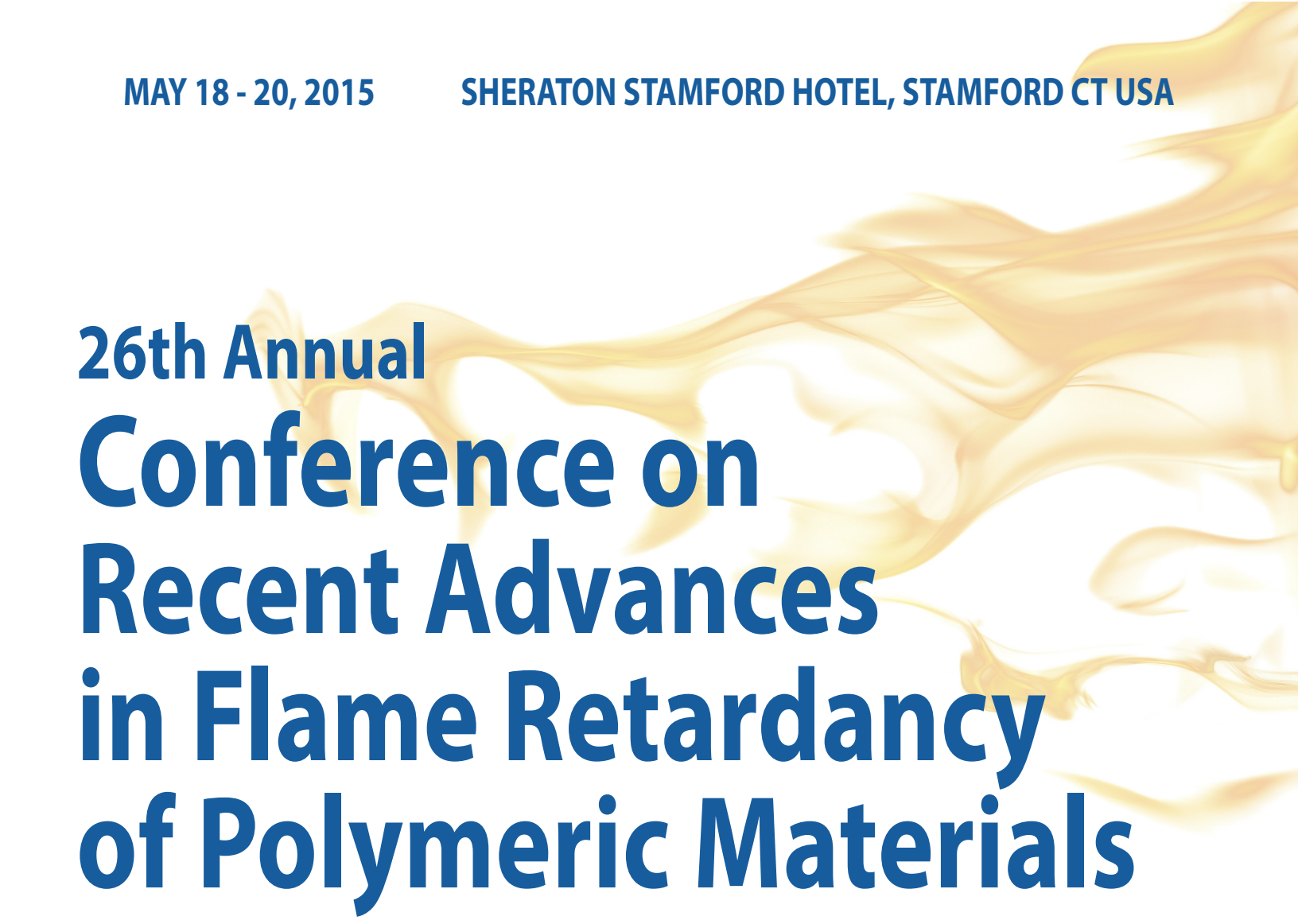
The epoxy composite samples displayed several different mechanisms of flame retardancy. Although the commercial flame retardant, TPP, exhibited potentially the best performance, the lignin and phos lignin specimen displayed intumescence and dense char formation respectively and all of the additives reduced the peak heat release and the total heat released during combustion. It was shown that with appropriate treatment with TPP that the epoxy can be made to char or intumesce instead of volatilizing upon degradation. However, lignin is a naturally charring material, so it is unclear whether the lignin or the epoxy behavior is the dominant cause of charring. Obviously there is a synergistic effect between the minimally charring epoxy and the naturally charring lignin to produce an intumescent protective layer that is not produced in either lignin or epoxy alone. Optimization and chemical explanation of this synergy should be investigated. Alternate strategies for using the high performing TPP seems also worthy of further investigation, particularly if one wants to reach the goal of HRR being below 100 kW/m^2 for high flame retardant effectiveness. Ultimately, further investigation into the chemistry and mechanisms of the lignin containing specimen during charring are warranted, to clarify proposed mechanisms and address poorly understood issues.

V. REFERENCES:

- (1) EPA, U. S. *Flame Retardants in Printed Circuit Boards*; Cincinnati, OH, 2014.
- (2) Levchik, S. V.; Weil, E. D. Thermal Decomposition, Combustion and Flame-Retardancy of Epoxy Resins - a Review of the Recent Literature. *Polym. Int.* **2004**, 53, 1901–1929.
- (3) Jang, B. N.; Wilkie, C. a. The Effects of Triphenylphosphate and Recorcinolbis(diphenylphosphate) on the Thermal Degradation of Polycarbonate in Air. *Thermochim. Acta* **2005**, 433, 1–12.
- (4) Do, M. Novel Efficient DOPO-Based Flame-Retardants for PWB Relevant Epoxy Resins with High Glass Transition Temperatures Y. *Polym. Adv. Technol.* **2008**, 507–515.
- (5) Weil, E. D. Mechanisms and Modes of Action in Flame Retardancy of Polymers. *Fire Retard. Mater.* **2001**, 31–68.
- (6) Mendis, G. P.; Hua, I.; Youngblood, J. P.; Howarter, J. a. Enhanced Dispersion of Lignin in Epoxy Composites through Hydration and Mannich Functionalization. *J. Appl. Polym. Sci.* **2014**, 41263, n/a – n/a.
- (7) Zhang, R.; Xiao, X.; Tai, Q.; Huang, H.; Hu, Y. Modification of Lignin and Its Application as Char Agent in Intumescent Flame-Retardant Poly (lactic Acid). *Polym. Eng. Sci.* **2012**.
- (8) De Chirico, a; Armanini, M.; Chini, P.; Cioccolo, G.; Provasoli, F.; Audisio, G. Flame Retardants for Polypropylene Based on Lignin. *Polym. Degrad. Stab.* **2003**, 79, 139–145.
- (9) Alalykin, a. a.; Vesnin, R. L.; Kozulin, D. a. Preparation of Modified Hydrolysis Lignin and Its Use for Filling Epoxy Polymers and Enhancing Their Flame Resistance. *Russ. J. Appl. Chem.* **2011**, 84, 1616–1622.
- (10) Hasburgh, L. E.; White, R. H.; Diitenberger, M. A.; Boardman, C. R.; Forest, U. S.; Forest, S.; Pinchot, O. G. Comparison of the Heat Release Rate from the Mass Loss Calorimeter to the Cone Calorimeter for Wood-Based Materials. In *Proceedings Fire and Materials 2015*; 2015; pp. 116–127.
- (11) Fiddler, W.; Parker, W. E.; Wasserman, a E.; Doerr, R. C. Thermal Decomposition of Ferulic Acid. *J. Agric. Food Chem.* **1967**, 15, 757–761.

MAY 18 - 20, 2015

SHERATON STAMFORD HOTEL, STAMFORD CT USA



26th Annual Conference on Recent Advances in Flame Retardancy of Polymeric Materials

CHAIRMAN

Charles Wilkie

Marquette University

Featuring presentations from outstanding scientists from around the world on topics covering the entire spectrum of flame retardancy. Topics include:

- Commercial Products
- Foams and Fabrics
- Nanocomposites
- Phosphorus
- New Flame Retardants and Specific Polymers
- Instrumentation

CONFERENCE COORDINATOR

Ariel Welch

Tel: (+1) 781-241-9084

Email: ariel.welch@bccresearch.com

BCC Research, 49 Walnut Park, Wellesley, MA 02481 USA
866-285-7215 (toll free in U.S. | (+1) 781-241-9084
ariel.welch@bccresearch.com | www.bccresearch.com
<http://www.linkedin.com/company/bccresearch.com>